

SULFUR IN COAL BY PROGRAMMED-TEMPERATURE OXIDATION

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ABSTRACT

A controlled-atmosphere, programmed-temperature, oxidation apparatus has been constructed and used to characterize organic-sulfur distribution in coals, partially desulfurized coals, and model systems. Samples were diluted with W_0 , and heated, in a stream of Ar containing 10% O_2 , at a programmed-temperature increase of $30^\circ\text{C}/\text{min}$. Concentrations of SO_2 , CO_2 , CO, O_2 , and H_2O in the effluent gas were continuously measured until the runs were completed at 1000°C . Evolution patterns produced by the oxidation products characterize the coal and, upon integration, provide total C-H-S analyses consistent with classical coal analysis methods. The SO_2 derived from coal pyrite evolves with a maximum at about 430°C , and that from the organic portion of coal produces principal evolution maxima at about 320°C (attributed to nonaromatic coal structures) and at about 480°C (attributed to aromatic structures). During oxidation the H/C ratio decreases with increasing temperature to about 0.6-0.7 at 400°C . The NMR spectrum of residue isolated to 400°C shows a sharp decrease in aliphatic carbon compared to the original coal.

INTRODUCTION

A number of precombustion chemical-beneficiation procedures have been developed that remove most of the inorganic sulfur (pyritic and sulfate) and some of the organic sulfur from coal. These have recently been reviewed by Morrison (1). A method to distinguish among the organic-sulfur functional groups or to classify the organic sulfur present in untreated or treated coals would be an asset to those involved in coal desulfurization research. The predictive value of such a method would also be useful in selecting coals that will be most improved by beneficiation methods. Calkins recently described pyrolysis experiments aimed at the determination of organic-sulfur-containing structures in coal and briefly reviewed work in this area (2). The present work is a continuation of our efforts toward an oxidative-degradation procedure useful for characterization of the organic sulfur in coal (3,4). A controlled-atmosphere, programmed-temperature oxidation (CAPTO) apparatus has been constructed and used to characterize organic-sulfur distribution in coals, partially desulfurized coals, and model systems. The system monitors the evolution of SO_2 , CO_2 , CO, O_2 , and H_2O from coal samples thermally degraded in the presence of oxygen and a solid diluent-oxidation catalyst. Distinctive patterns of SO_2 , CO_2 , and H_2O evolution during programmed-temperature oxidation provide insights into the structural characteristics of the organic matrix of coal samples.

EXPERIMENTAL

A diagram of the apparatus used in this study is shown in Figure 1. A mass-flow-controlled mixture of Ar (90 mL/min) and O_2 (10 mL/min) was passed through minus-200-mesh samples dispersed (1:30) in W_0 , (diluent-oxidation catalyst) and pre-positioned on quartz fibers (wool) near the center of a 1.2-cm (i.d.) x 72.2-cm vertical quartz combustion tube. A spring-loaded tube assembly held the combustion tube in position between neoprene seals. Samples were positioned at the midpoint of a 30.8-cm vertical tube furnace that surrounds the reaction tube. A microprocessor was used to temperature program the furnace (normally at a rate

of $30^{\circ}/\text{min}$). A type K dual-head, isolated-junction thermocouple extends through a quartz capillary rod (used to minimize dead volume) and is inserted into the center of the sample. One of the thermocouple signals was sent to a strip chart recorder, and the other, after amplification, to a digital data system. A quartz rod was inserted below the sample to reduce dead volume.

A 1.9-cm x 6.7-cm secondary furnace was mounted directly below the primary furnace. The reaction tube in the secondary furnace hot zone contains 3.0 g of WO_3 supported on quartz fibers. This furnace, maintained at 1050°C , was utilized to convert CO to CO_2 , and COS to CO_2 and SO_2 , and to maintain a constant SO_2/SO_3 ratio in the exit gas stream (5). A pressure transducer located just after the reaction tube continuously monitored the pressure of the system throughout the run.

The effluent gas flowed from the reaction tube through 1/16-in.-i.d. Teflon tubing to the infrared analyzers that continuously monitored the concentration of H_2O , SO_2 , CO_2 , and CO . A $\text{Mg}(\text{ClO}_4)_2$ drying tube located just after the H_2O analyzer removed H_2O from the gas stream before it entered the SO_2 analyzer. A CO analyzer was utilized; however, under normal operating conditions, all CO was converted to CO_2 . A paramagnetic oxygen analyzer was used for detection of the oxygen content of the effluent gas. A mass flow monitor was used to measure the total flow of the gas stream. All detector signals were sent to a multichannel strip chart recorder and a digital data system. The strip chart recorder provided immediate feedback on the progress of the experiment. The data system acquired raw data, applied corrections, integrated, and provided qualitative and quantitative information for the effluent gas components over any desired temperature range. These methods are described in an earlier report (4).

A typical experiment consisted of thoroughly mixing 200 mg of minus-200-mesh coal (dried at 105°C) with 6.0 g of WO_3 and drying the mixture in a vacuum oven at 100°C . A 3.0-g portion of WO_3 was placed on quartz wool in the combustion tube and positioned at the hot zone of the secondary furnace. The tube was placed in position, and the secondary furnace stabilized at 1050°C . The analyzers were standardized and the sample was added to the combustion tube. A flow of 90 mL/min Ar and 10 mL/min O_2 was continued as the sample was heated from ambient temperature to 1000°C at a rate of $30^{\circ}/\text{min}$.

RESULTS AND DISCUSSION

The CAPTO instrumentation provides time-resolved data for the concentration of SO_2 , CO_2 , CO , H_2O , and O_2 in the effluent gas stream as a sample is oxidized at a programmed rate of temperature increase. The total flow, the pressure, and the temperature are also monitored throughout the oxidation. The gas composition profile with increasing temperature for untreated Indiana Minshall coal is shown in Figure 2. Similar information has been obtained from other coals, model sulfur systems, and pyrite. Initially, several heating rates, flow rates, compositions of the O_2 - Ar mixture, diluents, and sample/diluent ratios were examined (3,4). Variation of gas evolution patterns with particle size was also studied. Particle size studies (minus-48-mesh x 0; minus-100-mesh x 0; minus-400-mesh x 0) were completed on Pittsburgh Seam (Ohio No. 8) and several other coals. Little or no change in gas evolution patterns with increasing temperature was noted over the particle size range studied.

Temperatures of Sulfur Dioxide Evolutions from Coals

The SO_2 evolution temperature maxima of seven coals oxidized using the CAPTO unit are shown in Table 1. A few show small SO_2 evolutions in the 170°C - 200°C region. This is consistent with the presence of sulfur and/or volatile sulfides that sublime up to 200°C and are oxidized by the secondary furnace to produce SO_2 evolution maxima. Principal SO_2 evolution maxima occur in three

temperature ranges centered near 320°C, 430°C, and 480°C. So that these SO₂ evolution maxima could be assigned to coal structures, the CAPTO unit was used to oxidize (1) coal treated to partially remove pyrite, (2) coal pyrite, and (3) a series of model sulfur-containing systems. Figure 3 compares the CAPTO results of untreated (ROM) and treated (Float 1.60; Float 1.30; ASTM HNO₃) Pittsburgh Seam coal. Each sample contained a different pyrite concentration. The sharp peak at 430°C decreases with decreasing pyrite concentrations and was tentatively assigned to SO₂ evolution from the coal pyrite. A Deister table sample of coal pyrite obtained from the Robena Mine and oxidized using the CAPTO unit shows sharp SO₂ evolution at 430°C and confirms the above assignment.

A series of sulfur-containing model systems (6) was oxidized in the CAPTO unit, and the SO₂ evolution maxima temperatures were recorded. The results are summarized in Table 2. Note that polythiophene, polydibenzothiophene, polyarylsulfides, and polyarylsulfones all show SO₂ evolution maxima temperatures of 450°C or greater. All of these evolutions fall near or above the highest SO₂ evolution maxima observed from coals oxidized in the CAPTO unit. Poly(thiophene-tetrahydrothiophene) shows two SO₂ evolution maxima temperatures (300°C and 475°C). This polymer contains alternating cyclic sulfide and thiophenic sulfur structures. The lower temperature SO₂ evolution is ascribed to oxidation of the cyclic sulfide structure; and the higher temperature evolution, present in approximately an equal amount, to oxidation of the thiophenic structure. Based upon the model system results, the principal coal SO₂ evolution maximum near 320°C is consistent with nonaromatic sulfide oxidation, and the principal maximum near 480°C is consistent with thiophenic, aryl sulfide, and aryl sulfone oxidation.

Quantitative Evaluation of the Effluent Gas Components

The CAPTO unit was initially constructed to characterize partially desulfurized coals produced from Pittsburgh Energy Technology Center oxydesulfurization experiments (7). These oxydesulfurized coals had most of the pyrite and 40%-60% of the organic sulfur removed; however, most of the mineral matter was retained. Figure 4 shows the CAPTO data for oxydesulfurized (pyrite-free) Indiana Minshall coal. The higher temperature SO₂ evolution maximum is broadened and shifted to a somewhat lower temperature (centered at 450°C). The atomic H/C and C/S ratios with progressive oxidation are calculated and plotted from continuous measurements of the H₂O, CO₂, and SO₂ concentrations in the effluent gas stream. A plot of these ratios for the oxydesulfurized Indiana Minshall coal is reported in Figure 5. The H/C ratio is abnormally high near the beginning of the oxidation due to H₂O released from the mineral matter along with H₂O produced from coal oxidation. The H/C ratio at the 320°C SO₂ evolution maximum is about 2.40 and that for the evolution centered at 450°C is about 0.40. The H/C ratio decreased to 0.7 at 400°C. This sharp decrease in H/C ratio up to 400°C was observed for all coals oxidized in the CAPTO unit for which the H/C ratio was plotted.

The oxydesulfurized Indiana Minshall coal was also oxidized in the CAPTO unit up to a maximum temperature of 400°C, and the oxidized coal was separated (float-sink) from W₀₃. The ¹³C CP-MAS NMR of the product is shown in Figure 6. A sharp decrease in aliphatic carbon is noted, but the coal has not been deeply oxidized. The SO₂ evolution maximum observed near 320°C must be associated with loss of these nonaromatic coal structures. Additionally, the SO₂ evolution observed beyond 400°C must be associated with oxidation of the aromatic coal structures. Integration of the SO₂ data up to 400°C and beyond 400°C reveals that 41% of the sulfur is associated with loss of nonaromatic carbon and about 59% is associated with oxidation of aromatic carbon. Similar data have been tabulated (Table 3) for a number of pyrite-free coals. The results for poly(thiophene-tetrahydrothiophene) are also presented in Table 3. A bimodal SO₂ evolution pattern exists and approximately one-half of the sulfur was lost up to 400°C. This is consistent with SO₂ evolution from oxidation of nonaromatic carbon followed by oxidation of the aromatic structures.

The total C-H-S content can be calculated from the integrated data. The unit was not specifically designed to provide elemental analysis results; however, the values serve as indicators of complete oxidation. The analytical results of four oxydesulfurized coals oxidized in the CAPTO unit are shown in Table 4 and are in good agreement with classical coal analyses results of these coals.

Gravimelt-Treated Coals

The CAPTO apparatus has been used to oxidize a number of raw and treated coals. The results provide information about the sulfur removed and remaining after coal beneficiation processes. Samples of untreated and Gravimelt-treated (8) Pittsburgh Seam coal were obtained from TRW. A portion of the untreated coal was treated with HNO_3 (1:9) overnight (ASTM Method) and washed until acid free. The untreated, HNO_3 -treated, and Gravimelt-treated coals were oxidized in the CAPTO unit. The results are shown in Figure 7. The untreated coal produces SO_2 evolution maxima at 320°C, 430°C, and 480°C. The 430°C SO_2 maximum due to pyrite is no longer present in the HNO_3 -treated coal. The Gravimelt-treated coal shows approximately the same SO_2 evolution at 320°C, but no 430°C SO_2 evolution is present, and the 480°C SO_2 evolution maximum has been strikingly diminished. The Gravimelt process appears to have removed the pyritic sulfur and most of the thiophenic and/or aryl sulfide sulfur. Integration of the SO_2 data up to 400°C (H/C ratio at 0.7) shows 55.5% of the remaining 0.75% coal sulfur to be nonaromatic, and integration beyond 400°C shows 44.5% in aromatic coal structures. The available analytical results for these coals are shown in Table 5. Note that the H/C ratio of the Gravimelt-treated coal is considerably below that of the untreated coal. This is consistent with the ^{13}C NMR results, which show a sharp increase in aromaticity (9).

CONCLUSIONS

Distinctive SO_2 evolution maxima are produced at about 320°C, 430°C, and 480°C for coals mixed with a diluent and oxidized at a programmed rate of temperature increase.

The SO_2 evolution maxima temperatures for coal have been correlated with those produced from the oxidation of model organosulfur-containing systems and pyrite. The coal SO_2 evolution near 320°C is ascribed to sulfur in nonaromatic structures; that near 430°C, to oxidation of pyrite; and that near 480°C, to oxidation of thiophenic and aryl sulfide type structures.

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DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1.
TEMPERATURES OF SULFUR DIOXIDE EVOLUTION
MAXIMA FROM COALS

COAL	TEMPERATURES (°C)
<u>Middle Kittanning</u>	
Oxydesulfurized	320 --- 445
<u>Kentucky No. 11</u>	
ROM	320 450 490
<u>Indiana Minshall</u>	
ROM	295 440 490
Oxydesulfurized	310 --- 450
<u>Illinois No. 6</u>	
ROM	310 440 455
Oxydesulfurized	320 --- 440
<u>Upper Freeport</u>	
Float 1.40	322 --- 475
Oxydesulfurized	200 325 500
<u>Pittsburgh Seam</u> (Ohio No. 8)	
PETC (ROM)	180 320 430 475
PETC (Float 1.30)	325 440 485
TRW (ROM)	325 435 480
TRW (Gravimelt)	320 --- 492
TRW (ASTM-HNO ₃)	328 --- 488
<u>Pittsburgh Seam</u> (W. Va.)	
ROM	322 430 475
ASTM-HNO ₃	170 322 480

TABLE 2.
TEMPERATURES OF SULFUR DIOXIDE
EVOLUTION MAXIMA FROM MODEL SYSTEMS

MODEL SYSTEMS	TEMPERATURES (°C)
<u>Thiophenes</u>	
Polythiophene	450
Polydibenzothiophene (Grignard)	540
Polydibenzothiophene (AlCl ₃)	540
Poly(thiophene-tetrahydrothiophene)	300 475
Poly(thiophene-benzene)	540
<u>Aryl Sulfides</u>	
Poly(diphenylsulfide-benzene)	550
3,3'-Thiobis(7H-Benz[de]Anthracen-7-one)	530
<u>Aryl Sulfones</u>	
Poly(p-phenylene Ether Sulfone)	540
<u>Sulfate</u>	
Ferrous Sulfate	620

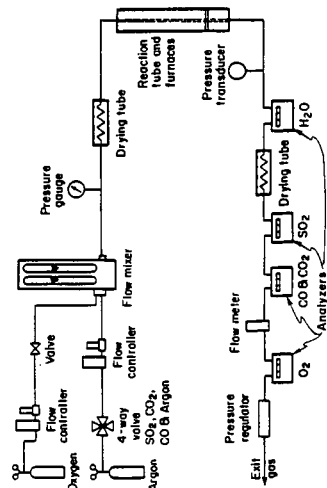


Figure 1. Controlled-atmosphere, programmed-temperature apparatus flow system.

FIGURE 2.

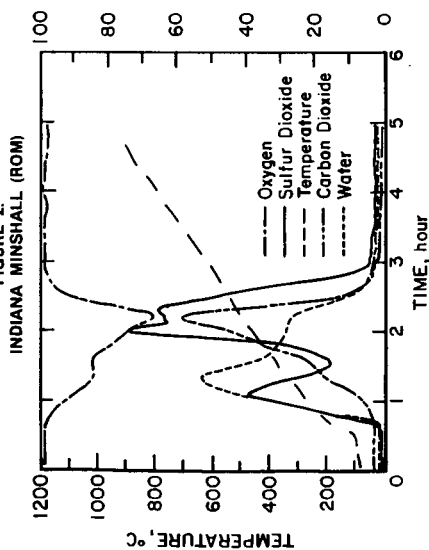


FIGURE 3.

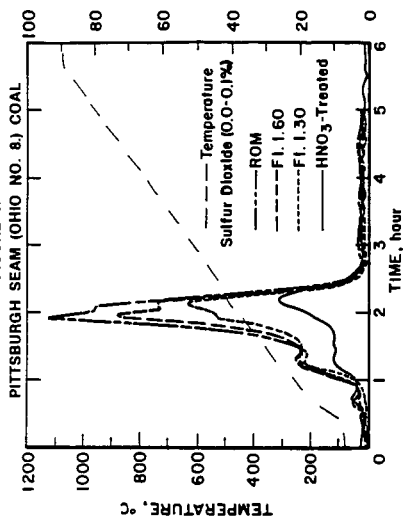


FIGURE 4.

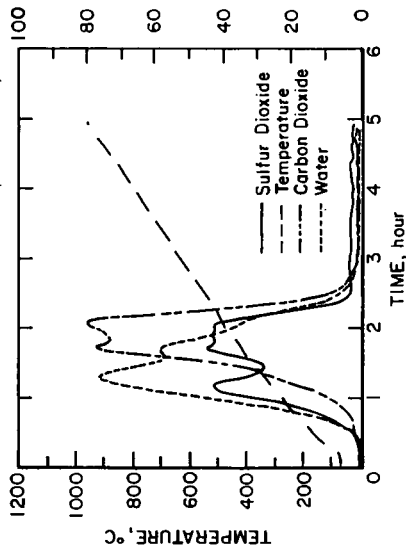


FIGURE 5.

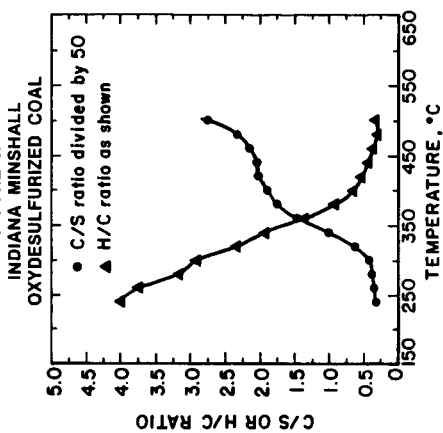


FIGURE 6.
¹³C NMR OF INDIANA MINSHALL COAL

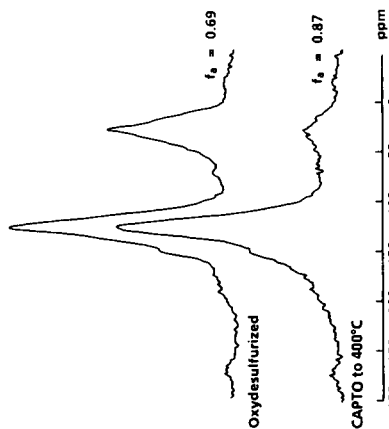


TABLE 3.
 NONAROMATIC -- AROMATIC SULFUR

COAL	NONAROMATIC	AROMATIC	SULFUR (%)	
			CAPTO	COAL ANALYSIS
Upper Freeport				
Float 1.40	21.7	78.3	0.38	0.60
Pittsburgh Seam (Ohio No. 8)				
TRW Gravimelt	55.5	44.5	0.75	0.75
TRW Starting Coal (ASTM-HNO ₃)	25.4	74.6	2.02	---
Pittsburgh Seam (W. Va.)				
(ASTM-HNO ₃)	30.4	69.7	1.39	---
Indiana Minshall				
Oxydesulfurized	41.4	58.6	2.42	2.50
Middle Kittanning				
Oxydesulfurized	34.7	65.3	0.73	0.67
Illinois No. 6				
Oxydesulfurized	50.9	49.1	2.27	2.42
Poly (Thiophene-Tetrahydrothiophene)	51.5	48.5	36.67	35.75

FIGURE 7.
 PITTSBURGH SEAM (OHIO NO. 8) COAL

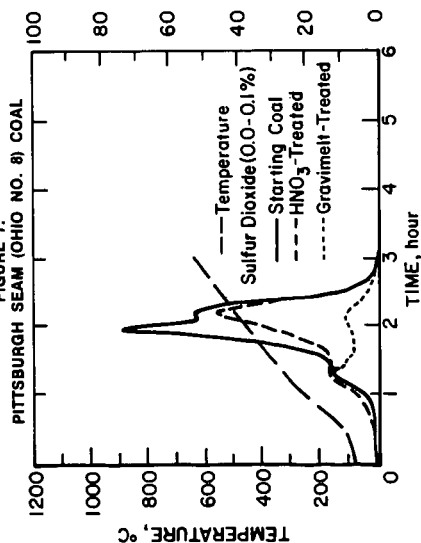


TABLE 4.
ANALYSIS OF OXYDESULFURIZED COALS
(moisture-free)

COAL	TREATMENT	METHOD	ASH %	C %	H %	S %	H/C	C/S
Indiana	None	Coal Anal.	14.7	61.0	4.5	6.3	0.88	26
Minshall	Oxydesulf.	Coal Anal.	13.1	64.0	4.2	2.5	0.78	69
Rank: HvBb	Oxydesulf.	CAPTO	---	67.0	4.2	2.4	0.74	74
Illinois	None	Coal Anal.	11.6	68.4	4.6	3.7	0.80	49
No. 6	Oxydesulf.	Coal Anal.	9.77	65.7	4.3	2.4	0.79	72
Rank: HvCb	Oxydesulf.	CAPTO	---	67.1	4.3	2.2	0.79	81
Middle	None	Coal Anal.	16.9	64.6	4.4	1.1	0.81	160
Kittanning	Oxydesulf.	Coal Anal.	16.2	61.9	4.0	0.67	0.77	247
Rank: HvCb	Oxydesulf.	CAPTO	---	63.3	4.0	0.60	0.75	280
Upper	None	Coal Anal.	16.2	72.3	4.3	1.6	0.71	122
Freeport	Oxydesulf.	Coal Anal.	15.3	72.0	4.2	0.76	0.70	253
Rank: Mvb	Oxydesulf.	CAPTO	---	70.4	4.1	0.71	0.69	265

TABLE 5.
TRW GRAVIMELT-TREATED
PITTSBURGH SEAM (OHIO NO. 8) COAL

Coal	Analytic Method	Ash	Total S	%C	%H	H/C	C/S
Raw *	Coal Anal.	10.15	4.22	---	---	---	---
Raw	CAPTO	---	3.93	73.1	5.1	0.83	50
HNO ₃	CAPTO	---	2.02	71.2	4.8	0.81	94
(ASTM)							
**	Coal Anal.	1.26	0.75	---	---	---	---
**	CAPTO	---	0.75	84.7	4.1	0.57	303

*Raw coal was analyzed as containing 0.20% sulfate sulfur, 1.78% pyritic sulfur, and 2.24% organic sulfur.

**Coal was treated at 370°C with 80/20 NaOH/KOH melt. Product was washed with water, 10% H₂SO₄; filtered; and washed 2 times with water.